Formaldehyde in Maple Sirup: An Adaptation of the Nash Method

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The Nash method for formaldehyde, based on formation of a yellow product when formaldehyde reacts with acetylacetone and an ammonium salt, was applied to maple sirup. A procedure was developed for separating the formaldehyde from the sirup. A constant blank value of 0.9 ppm of formaldehyde was established. Best results are obtained with sirups containing less than 6 ppm of formaldehyde. Collaborative study is planned.

A new development in the production of maple sap is the use of a germicidal pellet of paraformaldehyde to control microbial growth in the maple tree taphole. This development has brought about the need for an analytical method to measure trace amounts of formaldehyde that may occur in maple sirup made from sap obtained from the paraformaldehyde-treated tapholes. Because of the low solubility of the paraformaldehyde pellets, 72% of the samples tested contained less than 1 ppm formaldehyde. This dissolved formaldehyde is essentially removed by evaporation (boiling at atmospheric pressure) along with the vast quantities of water, 30–40 gallons for each gallon of sirup, that are vaporized during the hour and a half required to boil down the sap. Reported residues of formaldehyde in these sirups (1) are usually less than 1 ppm. Determining this very small concentration of formaldehyde requires that the method not only be accurate for determining trace amounts, but it must also be specific for formaldehyde. The method must not measure other carbonyl compounds, especially those of low molecular weight, that are present in maple sirup principally as a result of the alkaline degradation of hexose sugars. In the search for a satisfactory method Dr. John C. Speck, Jr., Michigan State University, suggested that the method developed by Nash (2) would meet the requirements.

The Nash method for formaldehyde was developed to measure quantitatively the trace amounts of formaldehyde in bacterial suspensions. This colorimetric method is based on the formation of a stable yellow product that results when traces of formaldehyde are added to approximately neutral solutions of acetylacetone and an ammonium salt. Formation of the colored product is due to the synthesis of diacetyldihydrolutidine (DDL). This colored product, DDL, has a strong absorption maximum at 415 mμ.

The method of Nash was adapted to the analysis of maple sirup for formaldehyde by developing a procedure for separating the formaldehyde from the sirup and establishing the limits of reliability and the limits of formaldehyde concentrations.

METHOD

Apparatus

(a) *Distillation apparatus.*—Consisting of a 30 ml micro Kjeldahl flask fitted with 19/38 ⅋ outer joint and a 4″ water-cooled West condenser[3] with a 19/38 ⅋ inner joint bent at a 90° angle (Fig. 1).

(b) *Micro burners.*

(c) *Receivers.*—5 ml graduates with funnel tops.

(d) *Spectrophotometer.*—Suitable for measuring absorption at 415 mμ; with matched 1 cm cells or matched test tubes.

(e) *Water bath.*—Capable of maintaining a temperature of 37 ± 1.0°.

Reagents

(a) *Nash's Reagent "B".*—(*1*) 150 g ammonium acetate (2*M*). (*2*) 3 ml acetic acid

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[3] Mention of a specific company or product does not constitute endorsement by the Department over other companies or products not mentioned.

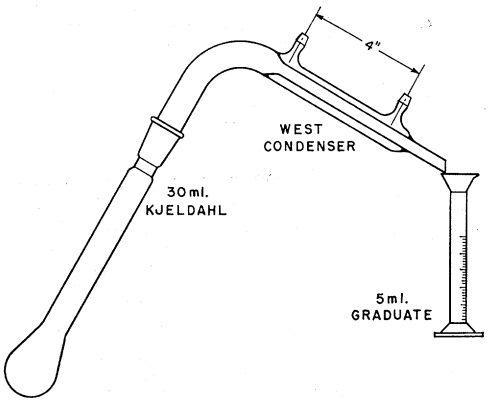

Fig. 1—Apparatus for distillation of formaldehyde from maple sirup.

(0.05*M*). (*3*) 2 ml acetylacetone (0.02*M*). Add (*1*), (*2*), and (*3*) to a 1000 ml volumetric flask, dissolve in 200–300 ml water, and dilute to mark.

(b) *Formaldehyde.*—37%.

(c) *Antifoaming agent.*

Determination

Weigh 20 ± 0.20 g of the sirup sample into a tared 30 ml micro Kjeldahl flask. Add 2 drops of an antifoaming agent and connect the West condenser. Mount the apparatus at an oblique angle and heat the flask with a micro burner previously adjusted to distill 3 ml water from sirup in 12–14 minutes. Collect 3 ml of the distillate in the 5 ml graduate. Transfer 1 ml of the distillate, using a 1 ml transfer pipet, to a 13 mm i.d. test tube. Add 1 ml water and 2 ml Nash's reagent. Heat the mixture in the test tube for 30 minutes in a water bath maintained at 37 ± 1° to develop the color. Transfer the colored solution to a 1 cm spectrophotometric cell and measure the absorbance at 415 mμ.

Blanks

To determine the absorbance due to the reagents, substitute 1 ml water (of the same source as that used in the formaldehyde determination) for the 1 ml sample distillate. Subtract the absorbance of the blank from that for the sample to obtain the absorbance due to the formaldehyde. Or, as a simpler procedure, measure the absorbance of the sample with the instrument adjusted to zero absorbance for the blank.

Obtain the concentration of formaldehyde in the sirup from the absorbance by using a standard curve or an equation.

Standard Curve

Construct a standard curve by plotting absorbances obtained for sirups containing formaldehyde *vs.* the known concentration of the added formaldehyde in ppm. Prepare the standard sirups to contain 1, 2, 4, 6, and 8 ppm formaldehyde, respectively, by adding the required amounts of aqueous solutions of formaldehyde, from stock solutions of appropriate concentrations, to 500 g aliquots of sirups. Choose appropriate concentrations of the aqueous stock solutions and add formaldehyde in 5 or 10 ml amounts to the sirup. (The pipet volume error and the sirup dilution error are negligible.) Be careful to mix formaldehyde and sirup completely (concordant results of triplicate analyses will confirm this).

A straight line relationship will be obtained for the standardization curve. Project this line to the Y axis (absorbance); the Y intercept indicates the blank for the sirup. Since the sirup used in constructing a curve from the absorbance values may be atypical, draw and use a parallel curve with zero intercept. Correct ppm values obtained from this curve for the sirup blank. This correction value is 0.9 ppm.

Since the standardization curve is reproducible and is a straight line, the standardization curve for formaldehyde may be expressed:

$$x = (y - 0.046)/0.060$$

where x = ppm; y = optical absorbances; 0.046 = a, the Y axis intercept (absorbance due to sirup and reagent blank); 0.060 = b, the slope of the curve factor.

This equation corrects for sirup and reagent blanks. To obtain the corrected ppm of formaldehyde in the test sirup, substitute the absorbance for 1 ml distillate reacted with the reagent for y in the above equation.

Discussion

In this method for the determination of formaldehyde in maple sirup it is not required that the formaldehyde be quantitatively distilled from the sirup and collected in the 3 ml of distillate; under similar distillation rates and distillate volumes there is a partition between the concentration of formaldehyde remaining in the sirup and the amount in the distillate. This partition coefficient is constant for concentrations of less than 6 ppm of formaldehyde in sirups. Thus, the distillation time should be kept constant to 13 minutes ± 1 minute and the

Table 1. Precision and accuracy of the modified Nash method for formaldehyde in maple sirup

Formaldehyde Concentration in Standard Sirups, ppm	Results by Modified Nash Method[a]				
	n	Range of Values, ppm	$\bar{x}$	S	Confidence Limits
1	13	1.00–1.20	1.09	0.079	±0.05
2	9	1.55–2.30	2.03	0.256	0.16
4	7	3.81–4.08	3.94	0.101	0.09
6	10	5.40–6.55	5.91	0.399	0.23
8	10	7.57–9.80	8.33	0.63	0.46

[a] n = number of analyses.
$\bar{x}$ = average value of n determinations.
S = standard deviation from the mean.

volume should be 3 ± 0.2 ml. The 1 ml of distillate taken for analysis, however, must be measured quantitatively.

While the method of Nash is highly specific for the determination of formaldehyde, a significant though very low blank is obtained for maple sirup even when it is known to have no formaldehyde added to it. This sirup blank may be caused by (*a*) a trace of formaldehyde that is possibly a normal constituent of maple sirup, or (*b*) some other aldehyde, derived from degraded sugars or organic acids, that reacts to yield DDL. The blank value of 0.9 ppm of formaldehyde was established by using a wide variety of sirups known not to have been in contact with formaldehyde.

The reproducibility, precision, and accuracy obtained by the adaptation of the Nash method for the analysis of maple sirups having different concentrations of formaldehyde are shown in Table 1. These data show that the method gives highest precision and accuracy when applied to the analysis of sirups containing less than 6 ppm.

In distilling the maple sirup in the 30 ml Kjeldahl flask, foaming may be a problem, but it is easily corrected by using such antifoaming agents as Wesson oil, Dowex Antifoam A, Atmos 300, and butter. Addition of one or two drops of these antifoaming agents to the sirup did not interfere with the determination.

Recommendation

It is recommended that the modified Nash method for formaldehyde in maple sirup be tested collaboratively.

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